

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property  
Organization  
International Bureau



(43) International Publication Date  
13 October 2005 (13.10.2005)

PCT

(10) International Publication Number  
WO 2005/094501 A2

(51) International Patent Classification: Not classified (81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SM, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

(21) International Application Number: PCT/US2005/009721

(22) International Filing Date: 23 March 2005 (23.03.2005)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data: 10/806,922 23 March 2004 (23.03.2004) US

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(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LT, LU, MC, NL, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:  
— without international search report and to be republished upon receipt of that report

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: BATTERY PASTE ADDITIVE AND METHOD FOR PRODUCING BATTERY PLATES

TYPE OF LEAD-ACID BATTERY PLATE PASTE MIX	LEAD OXIDE	MICRONIZED TTBLS ADDITIVE	WATER	SULFURIC ACID	FLOCK	EXPANDER
AUTOMOTIVE POSITIVE PLATE PASTE	1071 KG (79.52% WEIGHT)	10.71 KG (0.79% WEIGHT)	140 KG (10.39% WEIGHT)	125 KG (9.28% WEIGHT)	0.5 KG (0.02% WEIGHT)	0
AUTOMOTIVE BATTERY NEGATIVE PASTE	1071 KG (78.30% WEIGHT)	10.71 KG (0.79% WEIGHT)	140 KG (10.23% WEIGHT)	135 KG (9.86% WEIGHT)	0.5 KG (0.03% WEIGHT)	10.71 KG (0.79% WEIGHT)
INDUSTRIAL POSITIVE PLATE PASTE	1071 KG (80.09% WEIGHT)	10.71 KG (0.80% WEIGHT)	135 KG (79.52% WEIGHT)	120 KG (8.98% WEIGHT)	0.5 KG (0.04% WEIGHT)	0
INDUSTRIAL BATTERY NEGATIVE PASTE	1071 KG (79.41% WEIGHT)	10.71 KG (0.79% WEIGHT)	130 KG (9.64% WEIGHT)	115 KG (8.53% WEIGHT)	0.5 KG (0.04% WEIGHT)	21.4 KG (1.59% WEIGHT)

(57) Abstract: A battery paste additive, and process for making the same comprising micronized seed crystals of tetra basic lead sulfate, is added to battery paste and results in accelerated curing time and other improvements in battery performance. The battery paste additive may be used to produce positive or negative battery plates and may be used with conventional mixing, pasting and curing processes and equipment.

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Title: BATTERY PASTE ADDITIVE AND METHOD FOR PRODUCING BATTERY PLATES

The present invention relates generally to battery pastes and the curing process for battery plates. In particular, an improvement to battery paste and the curing process for battery plates for lead acid batteries is disclosed. More specifically, the present invention comprises a battery paste additive of micronized tetra basic lead sulfate crystals used to promote formation of additional tetra basic lead sulfate in the paste and plates. As a result, the curing process is accelerated and the resultant positive and negative battery plates have improved performance characteristics.

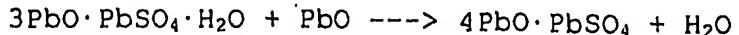
Background of the Invention

Traditional methods for producing battery plates for lead-acid batteries generally involve a mixing, curing and drying operation in which the active materials in the battery paste undergo chemical and physical changes that are used to establish the chemical and physical structure and subsequent mechanical strength necessary to form the battery plate. To produce typical battery plates, materials are added to commercial paste mixing machines common in the industry in the order of lead

oxide, flock, water and sulfuric acid, which are then mixed to a paste consistency. During mixing, chemical reactions take place in the paste producing basic lead sulfates, the most common of which is tribasic lead sulfate. The final paste composition is a mixture of basic lead sulfates, unreacted lead monoxide and residual free lead particles. Pasting is the process of making a battery plate from the paste mix. This paste is dispersed into a commercial automatic pasting machine of a type common in the industry which applies the paste to a grid structure composed of a lead alloy. The paste is dispensed into a hopper on the pasting machine and from there the paste is applied to the grids at high speed. The paste plates are generally surface dried in a tunnel dryer of a type common in the industry and then either stacked in columns or placed on racks. The stacked or racked plates are then placed in curing chambers. In these chambers the plates are subjected to temperatures of 70°C-80°C in a high humidity atmosphere to convert the tribasic lead sulfate in the plates to tetra basic lead sulfate and to allow oxidation of the residual free lead. The finished plates are now ready for assembly into batteries.

Two key factors important in the curing process are the formation of a proper crystal structure by converting tribasic lead sulfate (TRBLS) formed during paste mixing into tetra basic lead sulfate (TTBLS), and the formation of tetragonal lead oxide

by oxidizing residual free lead metal. Generally, a crystal structure high in tetra basic lead sulfate will increase battery life. The general formula for converting tribasic lead sulfate to tetra basic lead sulfate is set forth below:



A common problem with traditional battery paste compositions and methods for curing is that the chemical characteristics of the resultant plates are not uniform, varying in quality. Other common problems include difficulty in the repeatability of production, uncertain and/or lengthy curing time, the large number of curing chambers needed to process plates, and high capital and energy costs.

Consequently, a need exists for improvements in battery pastes which may be used with conventional paste mixing and curing processes, procedures and equipment to produce positive and/or negative battery plates having greater uniformity, more consistent quality, more consistent reproducibility, requiring shorter and more consistent curing times, requiring less curing chambers to process the plates and less capital and energy costs than traditional positive and/or negative battery plate pastes and methods of paste mixing and curing.

The present invention overcomes the disadvantages and/or shortcomings of known prior art battery pastes and curing

methods for battery plates and provides a significant improvement thereover.

Summary of the Invention

A battery paste additive comprising micronized crystals of tetra basic lead sulfate and a method of producing the battery paste additive and battery plates is disclosed herein. The battery paste additive is added to a battery paste to promote and increase formation of tetra basic lead sulfate (TTBLS) crystals during paste mixing and curing. The battery paste additive may be used with conventional paste mixes and paste mixing and curing procedures and equipment to improve battery plate production and the resulting battery plates.

Accordingly, an object of the invention is to provide a battery paste additive comprising micronized tetra basic lead sulfate crystals.

Another object of the invention is to provide a battery paste additive that will reduce the time to cure the paste into the battery plate.

Yet another object of the invention is to provide a battery paste additive that may be used with conventional paste mixes and conventional mixing and curing procedures and equipment.

Yet another object of the invention is to provide a battery paste additive that improves the mechanical and physical strength of the resulting battery plate.

Yet another object of the invention is to create battery plates which are uniform in physical structure and quality.

Yet another object of the invention is to provide a battery paste additive allowing battery pastes and plates to be consistently reproducible.

Yet another object of the invention is to provide a battery paste additive which is used in battery pastes to produce plates that are cured in a reasonably consistent duration of time.

Yet another object of the invention is to provide a battery paste additive that may be used to produce positive battery plates.

Yet another object of the invention is to provide a battery paste additive which may be used to produce negative battery plates.

Yet another object of the invention is to provide a battery paste additive that reduces curing costs and capital costs associated with conventional curing procedures, and curing chambers.

Numerous other objects, features and advantages of the present invention will become readily apparent from the detailed description and from the claims which follow.

Brief Description of the Drawings

FIG. 1 is a chart of the components for the automotive and industry paste mixes for positive and negative plates to which the battery additive has been added.

FIG. 2 is a chart of the results of the effect of 1% (by weight of lead oxide) of the battery paste additive on industrial paste and plate curing for a first sample;

FIG. 3 is a chart of the results of the effect of 1% (by weight of lead oxide) of the battery paste additive on industrial paste and plate curing for a second sample;

FIG. 4 is a graph of the effect of 1% (by weight of lead oxide) of the battery paste additive for the sample of FIG. 2;

FIG. 5 is a graph of the effect of 1% (by weight of lead oxide) of the battery paste additive for the sample of FIG. 3;

FIG. 6 is a chart of the effect of 1% (by weight of lead oxide) of the battery paste additive on automotive paste and plate curing for a third sample;

FIG. 7 is a graph of the effect of 1% (by weight of lead oxide) of the battery paste additive for the sample of FIG. 6;

FIG. 8 is a chart of the effect of 1% (by weight of lead oxide) of the battery paste additive on automotive paste and plate curing for control samples without the additive;

FIG. 9 is a chart of the effect of 1% (by weight of lead oxide) of the battery paste additive on automotive paste and plate curing for a fourth sample;

FIG. 10 is a chart of the effect of 1% (by weight of lead oxide) of the battery paste additive on automotive paste and plate curing for a fifth sample;

FIG. 11 is a graph of the effect of 1% (by weight of lead oxide) of the battery paste additive for the fourth and fifth samples in FIGS. 9-10, compared to the control sample of FIG. 8;

FIG. 12 is a graph of the effect of 1% (by weight of lead oxide) of the battery paste additive on the initial capacity of industrial battery cells;

FIG. 13 is a chart of the results of the effect of 1% (by weight of lead oxide) of the battery paste additive on fourteen paste mixes at the end of the curing cycle;

FIG. 14 is a chart of the results of standard industry rating tests for automotive batteries using batteries with and without the battery paste additive.

#### Detailed Description of the Preferred Embodiment

While the invention is susceptible of embodiment in many different forms, there will be described herein in detail, preferred and alternate embodiments of the present invention. It should be understood however, that the present disclosure is to be considered an exemplification of the principles of the

invention and is not intended to limit the spirit and scope of the invention and/or claims of the embodiments illustrated.

As disclosed herein, a battery paste additive is made and is then added to battery paste to improve the processing and the performance of battery plates. The battery paste additive comprises micronized tetra basic lead sulfate seed crystals, preferably with a median particle size from approximately 0.5 to 5.0 microns (preferably approximately one micron). These seed crystals are produced by a slow method of sulfuric acid addition to lead oxide, preferably in the form of HT-100 lead monoxide (99% or greater orthorhombic lead oxide raw material which is produced in a high temperature barton reactor followed by particle segregation via air classification, and due to its high reactivity, reacts with sulfuric acid and forms predominantly TTBLS crystals, resulting in a high percentage of TTBLS) and water to form TTBLS crystals which are subsequently centrifuged, dried and micromilled to produce micronized TTBLS crystals. The resultant battery paste additive is added to the paste during mixing, at a dosing level of approximately 0.25% to 5.00% of the weight of lead oxide in the mix, to accelerate and increase formation of tetra basic lead sulfate from tribasic lead sulfate in a battery paste, before curing. The micronized small crystals of tetra basic lead sulfate act as seeds or nucleation sites for formation of more TTBLS during paste mixing. The seed

crystals eliminate the need for energy of crystallization, accelerating the conversion of tribasic lead sulfate to TTBLS.

Preferably, the above-described production of tetra basic lead sulfate crystals and milling process is used to produce micronized tetra basic lead sulfate crystals. The milling process breaks individual crystals into smaller particles. The resultant fine material of micronized TTBLS seed crystals may be used as a battery paste additive for greater production of TTBLS in the paste, as described in more detail below. Preferably, dry milling, without requiring the use of a grinding medium such as sand, is used to micronize the TTBLS crystals formed from the mixtures above. A hopper may be used to store and/or transfer the TTBLS product to the micromill. While a dry micromill process is described herein, any other methods known in the art for producing and/or separating fine particles of TTBLS may be used to produce the battery paste additive, so long as the advantages and features of the present invention are realized.

In the preferred embodiment of the present invention, after a first batch of micronized TTBLS crystals is made, a second batch of micronized TTBLS crystals is made in the same manner, except that the micronized TTBLS crystals from the first batch are added as a component in the second batch. The micronized TTBLS crystals initially produced by the above-described procedure (first batch) is then used as a component of a

subsequent mixture. As described below, the subsequent mixture is the same mixture as the initial mixture, with the addition of micronized TTBLS crystals. Use of the initial micronized seed crystals from the first batch in the subsequent mixture (second batch) to produce the micronized TTBLS seed crystal additive performs essentially the same function that the micronized TTBLS seed crystal additive provides in the paste, promoting formation of TTBLS, and results in higher and more consistent purity of the TTBLS crystals produced. The resultant product of the subsequent mixture (second batch) may then be used as a battery paste additive. In an alternative embodiment, the initial mixture alone, without making the subsequent mixture, may be used as a battery paste additive.

Initial Mixture: In general, the production of the micronized tetra basic lead sulfate crystal additive uses an initial mixture of 1-90% (preferably approximately 75%), by total formula weight water, at a temperature between 0-100°C (preferably between 50-100°C, and ideally approximately 90-100°C); 10-70% (preferably approximately 15-20%) by total formula weight lead oxide; and 0.05-12% (preferably approximately 3-7%) by total formula weight dilute sulfuric acid ( $H_2SO_4$ ) at a 1-99% concentration (preferably approximately at a 20-50% concentration, and ideally approximately at a 35%

concentration). The sulfuric acid is added at two different times, as discussed below.

The initial mixture may be mixed in a reactor according to the following preferred procedure. The water is added to the reactor, mixing is begun, and the water is heated to the desired temperature, preferably approximately 90-100°C. The reactor water is then acidified with approximately 0.05-2.00%, preferably 0.05%, by total formula weight dilute sulfuric acid until the water is acidified at a pH of approximately equal or less than 2. The lead oxide is then added to the acidified water. Approximately 5-10%, preferably 5%, by total formula weight dilute sulfuric acid is then added to the mixture by a slow constant rate of sulfuric acid solution addition, as described below. Once sulfuric acid solution addition has completed, when the pH reaches approximately 9.5-8.5, the resultant initial mixture is centrifuged to remove excess water, the solid product is dried in a dryer, and then run through a hopper and a micromill to produce micronized TTBLS crystals. The resultant product is micronized TTBLS crystals. The dried sample may then be analyzed, and may also be analyzed prior to being run through the hopper and micromill.

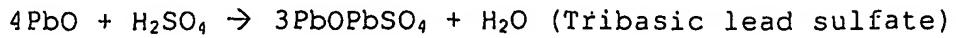
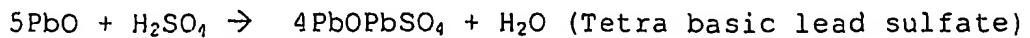
Preferably, the micronized TTBLS product from the initial mixture or first batch above is then used in a subsequent mixture or second batch to produce the micronized TTBLS crystals.

paste additive. The subsequent mixture (second batch) and procedure is identical to the initial mixture, except for the addition of 0.01-5.00% by total formula weight, preferably 0.01%, micronized TTBLS from the initial mixture (first batch), preferably added after the addition of lead oxide and prior to the addition of sulfuric acid, to the mixture. The same procedure described for the initial mixture (first batch) is followed in the subsequent mixture (second batch). The dried, micromilled product of the subsequent mixture (second batch) may then be used as a battery paste additive. Use of the micronized crystal product from the initial mixture (first batch) in the subsequent mixture (second batch) promotes formation of TTBLS, resulting in a higher percentage of TTBLS crystals (or purity) and more consistent purity of the TTBLS crystals produced than the micronized TTBLS produced from the initial mixture. Alternatively, the micronized TTBLS product from the initial mixture may be used as the battery paste additive.

Sulfuric Acid Solution Addition: The following procedure is preferable for both the initial and subsequent mixtures described above. The initial weight of sulfuric acid and the weight of the sulfuric acid in the reactor is recorded and monitored at incremental periods of time, preferably every half hour. With the temperature at approximately 90-100°C, sulfuric acid solution addition using approximately 35% sulfuric acid is

commenced and proceeds at a constant rate for approximately 2.5-4 hours. The total amount of sulfuric acid used in the addition process is approximately 5% by total formula weight.

Preferably, the sulfuric acid is added to the water/lead-oxide mixture slowly, at a constant rate of approximately 30-40lbs/hour, preferably 30lbs/hour, with vigorous mixing such that the rate of sulfuric acid addition allows for the formation of tetra basic lead sulfate. This slow addition of dilute acid favors the formation of tetra basic lead sulfate due to the localized in-situ stoichiometry providing an excess of lead oxide (PbO) molecules. By providing an environment rich with excess lead oxide molecules and dispersing the sulfuric acid rapidly due to vigorous mixing, a limited number sulfuric acid molecules favor formation of tetra basic lead sulfate, with each sulfuric acid molecule bonding with five (5) PbO molecules, as shown in the chemical reactions below. An addition rate of sulfuric acid which is too rapid may result in the formation of tribasic lead sulfate rather than tetra basic lead sulfate, as illustrated below.



After approximately two hours of sulfuric acid addition, the temperature, pH and weight of the sulfuric acid are monitored. The pH should preferably be approximately 10-11.

After approximately 2.5 hours of sulfuric acid addition, the reactor batch may be sampled every fifteen minutes to check the pH. The sulfuric acid addition is preferably stopped when the pH is approximately 8.5-9.5. The resultant TTBLS crystal product may be sampled and analyzed for properties including the amount of lead, pH and X-ray diffraction (XRD) analysis to measure the amount of lead sulfate and lead oxide in the sample. The product is then centrifuged, dried in drying pans and in a drier and analyzed for properties including particle size and humidity. Larger particles may be micromilled again to produce TTBLS crystals of the desired size.

The reaction of lead oxide (PbO) with sulfuric acid ( $H_2SO_4$ ) is exothermic and it is preferable to avoid boiling temperatures, such as those exceeding approximately 99-101°C as foaming and batch overflow may result. If the temperature exceeds approximately 99-101°C, cool water may be applied until the temperature drops to below approximately 95-99°C.

Preferably, the resultant dried TTBLS micronized seed crystals will have a lead content of approximately 90.5-93.3% lead oxide by weight and a TTBLS content of approximately 90% or more TTBLS by weight. The lead content of the product may be measured by EDTA titration and may be used to determine that the proper ratio of sulfuric acid has been added. The TTBLS content may be measured by x-ray diffraction and may be used to

determine the purity of the product. The resultant TTBLS product will also preferably have approximately 1.0% wt/wt or less moisture/humidity by weight, and a median particle size of approximately 0.5-5.0 microns, preferably one micron or less, and an appearance in color of tan yellow. TTBLS may discolor or blacken when exposed to ultraviolet light. It is therefore preferable to avoid extended exposure to UV light including sun and indoor lighting.

Although, a particular form of lead oxide, HT-100, which is high in orthorombic lead oxide, is preferred to produce the micronized seed crystals, any form of lead monoxide may be used. The resultant battery paste additive, when added to battery paste produces plates and batteries which have an increased battery life and performance, improved plate strength, and the processes for producing the additive and incorporating it into a battery paste are easily reproducible.

Although the addition of sulfuric acid to the initial and subsequent mixtures is preferably at a slow constant rate, such as that described above, other methods of sulfuric acid addition are foreseen, such as additions of sulfuric acid in multiple intervals, a slower rate of addition with less dilute sulfuric acid and/or a faster rate of addition with more dilute sulfuric acid. In addition, a continuous process in which sulfuric acid

and lead oxide are combined into a continuous unbroken stream, eliminating the need for batch processing.

Although the procedure for micronizing the TTBLS crystals, preferably requires centrifugation, drying, a hopper and a micromill, other methods of micronizing the TTBLS product are foreseen, such as crystal growth modification, sheer pumps, homogenization mills, cryogenic grinding and/or air classification. The use of other chemicals such as sodium sulfate is not required to produce a small particle size for the paste additive.

The resultant micronized TTBLS may be used as a battery paste additive by mixing approximately 0.25-5.00%, preferably approximately 1.0%, by weight of the lead oxide in the paste mix of the micronized TTBLS additive with conventional paste mixes using conventional paste mixers, pasting machines, tunnel dryers and curing chambers under standard conditions using standard manufacturing mixing and curing procedures.

#### Use of Micronized TTBLS Additive in Paste Mixing and Curing

Preferably, the amount of micronized TTBLS crystals added to the paste mix is approximately equal to 1.0% by weight of the lead oxide in the paste mix. An amount of micronized TTBLS crystals approximately equal to 1.0% by weight of the lead oxide in the paste mix is sufficient for use in both positive and negative plate paste mixes. The micronized TTBLS additive

promotes and increases the formation of more TTBLS in the paste. TTBLS formation occurs during mixing, pasting and/or curing. The reaction conditions determine the rate of formation of TTBLS during each of the mixing, pasting and curing stages. The rate of formation is dependent on factors such as the temperature and time to prepare the paste mix.

Conventional paste mixing generally occurs at a temperature of approximately 45-65°C. In conventional paste mixes, TTBLS generally is not formed because this temperature is too low. The present invention allows formation of TTBLS in the paste during paste mixing at these low temperatures, as low as approximately 50°C. Due to the paste additive, a substantial amount of TTBLS will be formed during the paste mixing even at a low temperature, reducing or eliminating the need for TTBLS formation during the curing process.

In conventional paste mixes, at temperatures lower than 60°C, additional formation is necessary during the curing process. Generally, tetra basic lead sulfate will also be formed at temperatures lower than approximately 60°C and can take place at approximately 40°C. However, at lower temperatures the rate of formation is reduced and the amount in the finished paste is also reduced. This can be offset by increasing the mixing time. This, however, increases the time

to produce a paste mix beyond the 20-30 minute range preferred by the battery industry.

In conventional curing, temperatures of approximately 70-80°C are required for formation of TTBLS. The present invention permits temperatures as low as 50°C to be used during curing. The present invention may also be used at higher temperatures, resulting in more rapid formation of TTBLS than in conventional pastes. Preferably, the battery pastes containing the TTBLS additive are cured at a temperature approximately equal to or less than 50°C.

Plates made from pastes containing the additive may be stacked or separated, but are not required to be separated, during the curing process. The use of a polymer to bind TTBLS crystals in the paste is not required.

The preferred embodiment of the invention may be used in a variety of battery applications, including but not limited to automotive and industrial battery plate production. The preferred embodiment of the present invention may be used with positive or negative battery pastes for production of either positive or negative battery plates.

The additive produces more TTBLS in the paste, speeds up conversion of TRBLS to TTBLS and improves plate to plate reproducibility. As a result of the decreased curing time

required due to the additive, fewer curing chambers are required to meet battery plate production requirements.

FIG. 1 is a chart identifying the amounts of each of the components of four lead-acid battery plate paste mixes prepared using the methods and additive described herein. The examples in FIG. 1 illustrate the addition of the above described battery paste additive to paste mixes for automotive and industrial battery plates in lead-acid batteries. For the automotive positive plate paste mix, the specific gravity of the sulfuric acid in the mixture examples is preferably approximately 1.400 and the paste density is typically in the range of approximately 4.15-4.27 g/cc. For the automotive negative plate paste mix, the specific gravity of the sulfuric acid is preferably approximately 1.400 and the paste density is typically in the range of approximately 4.27-4.39g/cc. For the industrial positive plate paste mix, the specific gravity of the sulfuric acid is preferably approximately 1.400 and the paste density is typically in the range of approximately 4.33-4.45 g/cc. For the industrial negative plate paste mix the specific gravity of the sulfuric acid is preferably approximately 1.400 and the paste density is typically in the range of approximately 4.45-4.57 g/cc.

The paste density is a measure of the composition of the paste and also of its suitability for being pasted by commercial

paste mixing machines for the positive or negative plate paste mix. Paste density is determined by measuring the weight of paste required to fill a cup having constant volume of 50 cubic centimeters. The "flock" component in FIG. 1 is a fibrous material, usually composed of polyester, nylon or modacrylic fibers, that is added to the paste to increase the mechanical strength of the pasted plate. The "expander" component in FIG. 1 is usually a mixture of barium sulfate, carbon black and lignosulfate, that is added to the negative paste to improve the performance and life of the negative plate.

Battery paste mixes of the type described in FIG. 1 were mixed and cured according to standard procedures using standard equipment with the exception of the addition of the additive. The particular mixes used and procedure for mixing and curing typically vary in the industry. The battery paste mixes in FIG. 1 represent typical paste mixes used in the industry with the exception of the addition of the additive. To each paste mix, the micronized TTBLS additive was added at 1% of the weight of lead oxide in the paste mix. The resultant industrial and automotive pastes and plates were tested at selected time intervals during the mixing and curing process against a control sample without the battery paste additive, the results of which are shown in FIGS. 2-11. The control samples were produced from a standard paste mix without the battery paste additive. The

resultant pastes and plates were tested using x-ray diffraction for the presence of several phases including the percent of TTBLS, TRBLS, tetragonal lead oxide, orthorhombic lead oxide and free lead. The resultant paste mix and cured plates using the additive demonstrated accelerated curing properties and were determined to promote greater formation of TTBLS than in pastes without the additive.

The data in FIGS. 2-14 represent results from positive battery plate mixes containing the battery paste additive in an amount equal to approximately 1% by weight of the lead oxide. Similar results were achieved in tests of negative plate paste mixes.

As can be seen in FIGS. 2-14, the resultant battery pastes with the additive demonstrated improved characteristics over known battery paste compositions. FIGS. 2 and 3 show in chart form the results of the effect of 1% of the battery paste additive on industrial paste and plate curing for a first sample (Figure 2) and second sample (Figure 3), versus a control sample. FIG. 2 presents data for five trials as well as the averages of those trials. FIG. 3 presents data for three trials of the paste with the additive as well as the averages, and one trial of the control sample. The charts shown in FIGS. 2 and 3 show the amount of tetra lead oxide, ortho lead oxide, tetra basic lead sulfate and tribasic lead sulfate at varying periods during

the paste mixing and curing process, measured in percent content amounts. FIG. 3 also shows the percent lead (Pb) content at varying periods during the paste mixing and curing process. The experimental samples demonstrated significantly higher tetra basic lead sulfate content at the time intervals between the end of paste mixing and during curing. As can be seen from the data in the figures, significantly greater TTBLS is formed during paste mixing, as well as during curing, in paste mixes containing the additive than those without the additive.

FIGS. 4 and 5 show in graph form the average results for the first and second samples respectively of the effect of 1% micronized TTBLS on industrial paste and plate curing versus the control sample, and show the percentage of tetra basic lead sulfate present in the paste and plate at varying periods during mixing and curing. The results of FIGS. 4 and 5 demonstrate a significantly higher percent of TTBLS in the paste and plate during curing in the samples containing the TTBLS crystal additive.

FIG. 6 shows in chart form the effect of 1% of the battery paste additive on automotive paste and plate curing of a third sample. The chart shown in FIG. 6 shows the amount of tetra lead oxide, ortho lead oxide, tetra basic lead sulfate and tribasic lead sulfate at varying periods during the paste mixing and curing process, measured in percent content. FIG. 6 also

shows the percent lead (Pb) content at varying periods during the paste mixing and curing process. The experimental samples having the additive demonstrated significantly higher tetra basic lead sulfate content at the time intervals between the end of paste mixing and during curing, for various trials, as well as the averages for those trials.

FIG. 7 shows in graph form the average results for a third sample of the effect of 1% micronized TTBLS on automotive paste and plate curing versus the control sample, and shows the percentage of tetra basic lead sulfate present in the paste and plate at varying periods during mixing and curing. The results of FIG. 7 demonstrate a significantly higher percent of TTBLS in the paste and plate during curing in the sample containing the TTBLS crystal additive.

FIGS. 9-10 show in chart form the effect of 1% of the battery paste additive on automotive paste and plate curing of a fourth sample and a fifth sample, versus a control sample in FIG. 8. The charts shown in FIGS. 8-10 show the amount of tetra lead oxide, ortho lead oxide, tetra basic lead sulfate and tribasic lead sulfate at varying periods during the paste mixing and curing process, measured in percent content. FIGS. 8-10 also shows the percent lead (Pb) content at varying periods during the paste mixing and curing process. The control samples in FIG. 8 represent different samples taken from the same paste mix at

different times. The experimental samples having the additive (FIGS. 9 and 10), demonstrated significantly higher tetra basic lead sulfate content than the control sample (FIG. 8), at the time intervals between the end of paste mixing and during curing, for various trials.

FIG. 11 shows in graph form the results for the effect of 1% micronized TTBLS on automotive paste and plate curing for a fourth and fifth sample, and show the average percentage of tetra basic lead sulfate present in the paste and plate at varying periods during mixing and curing. The results shown in FIG. 11 demonstrate a significantly higher percent of TTBLS in the paste and plate in the paste and during curing in samples containing the TTBLS crystal additive. FIG. 11 shows the results of two trials of a paste mix with the additive and one trial of a paste mix without the additive. As can be seen from the results of the two trials of the mix with the additive, the results were highly reproducible, and each had significantly higher percentages of TTBLS than the control sample.

FIG. 12 shows the effect of 1% micronized TTBLS on initial capacity of motive power industrial battery cells, versus a control sample, tested at the 5-hour rate of discharge (the current drain (85 Amps) that will completely discharge a typical battery in five hours) rate. It can be seen that the capacity of the cells containing 1% micronized TTBLS is superior to those

where conventional plates and paste formulas were used. A cycle is a battery discharge followed by a recharge.

FIG. 13 shows the results of 14 separate paste mixing, pasting and curing tests carried out for industrial paste mixes, demonstrating excellent reproducibility of the process. The paste mixes used are similar to the paste mixes described in FIG. 1, although variations of the mix formulas would give similar results. The tests were taken from the finished plates at the end of the curing process after twenty-four hours.

FIG. 14 shows a comparison of test data from three automotive batteries that were produced with the TTBLS additive and three automotive batteries without the TTBLS additive, and the average values for first, second and third reserve capacity, first, second and third cold cranking amps, and ampere hours at a 20 hour rate. It can be seen that the Cold Cranking Amperes, Reserve Capacity and 20-hour Rate Capacity were all improved in the batteries containing 1% micronized TTBLS additive in the paste used to produce the positive plates. The performance of automotive batteries is likewise improved when 1% micronized TTBLS additive is used in a negative paste mix for production of negative plates. These tests are standard industry rating tests for automotive batteries and are specified by the Battery Council International for testing automotive batteries.

In summary, as can be seen from the foregoing tests of the amounts of TTBLS and free lead oxide present in the battery paste mix at timed intervals during the mixing and curing process, the present invention produces highly favorable results, while at the same time overcoming the disadvantages and/or shortcomings of known battery paste materials. Such results are an improvement over known prior art battery pastes and battery paste materials; as well as the methods for producing the same.

The foregoing specification describes only the preferred embodiment and alternate embodiments of the invention. Other embodiments besides the above may be articulated as well. The terms and expressions therefore serve only to describe the invention by example only and not to limit the invention. It is expected that others will perceive differences, which while differing from the foregoing, do not depart from the spirit and scope of the invention herein described and claimed.

Claims

What is claimed is:

1. A chemical composition for addition to battery plate pastes, said chemical composition comprising:  
lead oxide; and  
sulfuric acid.
2. The composition of Claim 2, wherein the lead oxide and the sulfuric acid react to form tetra basic lead sulfate crystals.
3. The composition of Claim 2, wherein the TTBLS crystals are micronized.
4. A chemical composition for addition to battery plate pastes, said chemical composition comprising:  
a first complexing agent comprising tetra basic lead sulfate;  
a second complexing agent comprising a lead oxide; and  
a third complexing agent comprising sulfuric acid.
5. The composition of Claim 4, wherein said first complexing agent, said second complexing agent and said third complexing agent react to form tetra basic lead sulfate crystals.
6. The composition of Claim 4, wherein the lead oxide comprises lead monoxide.
7. The composition of Claim 4, wherein the sulfuric acid is dilute.

8. The composition of Claim 4, wherein the lead oxide is high in orthorhombic lead oxide content.

9. The composition of Claim 4, wherein the TTBLS crystals are micronized.

10. A method of producing an additive for a battery plate paste, comprising the steps of:

mixing together water and lead oxide;

mixing sulfuric acid into the water and lead oxide mixture to create TTBLS crystals.

11. The method of Claim 10, further comprising the step of micronizing the TTBLS crystals.

12. A method of producing an additive for a battery plate paste, comprising the steps of:

mixing together water and a lead oxide complexing agent to create a first substance;

mixing together the first substance with a tetra basic lead sulfate complexing agent to create a second substance;

mixing together the second substance with a sulfuric acid complexing agent to create TTBLS crystals.

13. The method of Claim 12, wherein the sulfuric acid is dilute.

14. The method of Claim 12, wherein the sulfuric acid is added at a slow constant rate, with vigorous mixing.

15. The method of Claim 12, wherein the lead oxide is high in orthorhombic lead oxide content.

16. The method of Claim 12, further comprising the steps of:

micronizing the TTBLS crystals.

17. The method of Claim 12, further comprising the steps of:

centrifuging the TTBLS crystals;

drying the TTBLS crystals; and

placing the TTBLS crystals through a micromill to create micronized TTBLS crystals.

18. The method of Claim 12, wherein the sulfuric acid adjusts the pH of the first substance.

19. The method of Claim 12, wherein the lead oxide comprises lead monoxide.

20. The method of Claim 12, wherein the TTBLS crystals comprise approximately 1-90% by total formula weight water, approximately 0.05-20% by total formula weight sulfuric acid, approximately 10-70% by total formula weight lead oxide, and approximately 0.01-5.00% by total formula weight tetra basic lead sulfate.

21. The method of Claim 20, wherein approximately 1-2% of said sulfuric acid is added to the water to lower the pH of the water to approximately equal or less than 2.

22. The method of Claim 21, wherein approximately 5-10% by total formula weight sulfuric acid is added to the first substance.

23. A battery paste, wherein the composition claimed in Claim 1 is added into battery paste mix.

24. A battery paste, wherein the composition claimed in Claim 4 is added into battery paste mix.

25. The battery paste claimed in Claim 24, wherein said battery paste is used to produce positive battery plates.

26. The battery paste claimed in Claim 24, wherein said battery paste is used to produce negative battery plates.

27. A method of producing a battery paste, said method comprising the steps of:

mixing together a lead oxide complexing agent and a tetra basic lead sulfate complexing agent to create a first substance;

mixing together water and a sulfuric acid complexing agent to create a second substance;

mixing together the first substance with said second substance to create a battery paste additive;

mixing together the battery paste additive with a battery paste mix.

28. A method of producing a battery plate paste, comprising the steps of:

creating a micronized tetra basic lead sulfate chemical composition; and

incorporating said chemical composition into a battery paste mix.

29. The method as claimed in Claim 28, wherein the tetra basic lead sulfate chemical composition comprises:

lead oxide;

sulfuric acid; and

water.

30. A battery paste additive comprising:

water;

lead oxide;

sulfuric acid; and

tetra basic lead sulfate.

31. The battery paste additive of Claim 30, wherein the additive comprises approximately 1-90% by total formula weight water, approximately 0.05-20% by total formula weight dilute sulfuric acid, approximately 10-70% by total formula weight lead oxide, and approximately 0.01-5.00% by total formula weight tetra basic lead sulfate.

32. The battery paste additive of Claim 30, wherein the additive promotes formation of tetra basic lead sulfate in a battery paste.

33. A method for making a battery plate, comprising the steps of:

mixing micronized tetra basic lead sulfate with a battery paste mix to create a battery paste; and  
curing the battery paste.

34. A battery plate made by the method of Claim 33.

35. The composition claimed in Claim 23, wherein said additive comprises approximately 0.25-5.00% by weight of the lead oxide in the paste mix.

36. The composition claimed in Claim 24, wherein said additive comprises approximately 0.25-5.00% by weight of the lead oxide in the paste mix.

**FIG. 1**

TYPE OF LEAD-ACID BATTERY PLATE PASTE MIX	LEAD OXIDE	MICRONIZED TTBL'S ADDITIVE	WATER	SULFURIC ACID	FLOCK	EXPANDER
AUTOMOTIVE POSITIVE PLATE PASTE	1071 KG (79.52% WEIGHT)	10.71 KG (0.79% WEIGHT)	140 KG (10.39% WEIGHT)	125 KG (9.28% WEIGHT)	0.5 KG (0.02% WEIGHT)	0
AUTOMOTIVE BATTERY NEGATIVE PASTE	1071 KG (78.30% WEIGHT)	10.71 KG (0.79% WEIGHT)	140 KG (10.23% WEIGHT)	135 KG (9.86% WEIGHT)	0.5 KG (0.03% WEIGHT)	10.71 KG (0.79% WEIGHT)
INDUSTRIAL POSITIVE PLATE PASTE	1071 KG (80.09% WEIGHT)	10.71 KG (0.80% WEIGHT)	135 KG (79.52% WEIGHT)	120 KG (8.98% WEIGHT)	0.5 KG (0.04% WEIGHT)	0
INDUSTRIAL BATTERY NEGATIVE PASTE	1071 KG (79.41% WEIGHT)	10.71 KG (0.79% WEIGHT)	130 KG (9.64% WEIGHT)	115 KG (8.53% WEIGHT)	0.5 KG (0.04% WEIGHT)	21.4 KG (1.59% WEIGHT)

**FIG. 2A**      **EFFECT OF 1% TTBLS ON INDUSTRIAL PASTE AND PLATE CURING – 1ST SAMPLE**

CONTROL SAMPLES					
SAMPLE	TRIAL	A-PBO (TETRA)	B-PBO (ORTHO)	TETRABASIC	TRIBASIC
PASTE AT END OF MIXING	1	58.0	2.6	0.0	39.4
	2	51.1	7.9	0.0	40.9
	3	59.4	2.2	1.2	37.2
	4	66.4	2.1	0.0	31.5
	5	50.2	1.1	2.4	46.3
	AVG	57.0	3.2	0.7	39.1
PASTE PLATE AT END OF TUNNEL DRYER	1	66.7	1.9	0.0	31.4
	2	59.2	8.5	5.7	26.6
	3	55.9	5.5	10.6	28.1
	4	61.8	4.8	2.1	31.3
	5	60.8	3.2	6.9	29.1
	AVG	60.9	4.8	5.1	29.3
PLATES AFTER 3 HOURS CURING	1	57.5	9.7	0.5	32.3
	2	61.2	10.7	0.0	28.8
	3	60.7	8.7	2.1	28.5
	4	60.4	9.8	1.0	28.7
	5	58.7	5.3	2.9	33.1
	AVG	59.7	8.8	1.3	30.3
PLATES AFTER 6 HOURS CURING	1	52.0	4.4	1.8	41.8
	2	57.1	9.1	0.0	33.7
	3	59.6	2.4	0.9	37.1
	4	54.4	8.2	1.6	35.8
	5	57.2	7.5	2.7	32.6
	AVG	56.1	6.3	1.4	36.2
PLATES AFTER 9 HOURS CURING	1	52.6	4.3	1.5	41.6
	2	67.7	2.3	1.9	28.2
	3	63.6	6.9	1.9	27.6
	4	60.2	10.4	2.3	27.2
	5	61.6	3.2	1.9	33.3
	AVG	61.1	5.4	1.9	31.6
PLATES AFTER 12/13 HOURS CURING	1	30.2	1.7	68.1	0.0
	2	59.1	10.3	4.6	26.0
	3	59.8	2.1	14.2	23.9
	4	64.9	2.3	11.0	21.8
	5	53.9	4.3	9.3	32.4
	AVG	53.6	4.8	21.4	26.0

**FIG. 2B**

EFFECT OF 1% TTBLS ON INDUSTRIAL PASTE AND PLATE CURING – 1ST SAMPLE

EXPERIMENTAL SAMPLES					
SAMPLE	TRIAL	A-PBO (TETRA)	B-PBO (ORTHO)	TETRABASIC	TRIBASIC
PASTE AT END OF MIXING	1	38.5	0.0	51.7	9.8
	2	34.1	0.7	57.7	7.5
	3	36.1	0.0	58.3	5.5
	4	40.2	0.0	55.1	4.7
	5	34.5	1.2	59.5	4.8
	AVG	36.7	0.4	56.5	6.5
PASTE PLATE AT END OF TUNNEL DRYER	1	81.9	8.1	10.1	0.0
	2	45.2	2.1	27.4	25.3
	3	44.1	1.6	29.9	23.9
	4	43.8	1.2	43.0	11.9
	5	48.6	3.4	19.5	28.5
	AVG	52.7	3.3	26.0	17.9
PLATES AFTER 3 HOURS CURING	1	26.2	2.2	71.6	0.0
	2	20.8	4.3	71.5	3.4
	3	34.6	3.4	57.4	4.6
	4	24.1	3.4	66.7	5.8
	5	36.9	1.9	51.3	10.0
	AVG	28.5	3.0	63.7	4.8
PLATES AFTER 6 HOURS CURING	1	25.3	2.9	71.8	0.0
	2	19.4	5.5	72.6	2.5
	3	31.0	2.0	67.0	0.0
	4	28.1	1.4	66.8	3.6
	5	32.6	1.7	65.6	0.0
	AVG	27.3	2.7	68.8	1.2
PLATES AFTER 9 HOURS CURING	1	26.7	4.5	61.7	7.0
	2	27.3	1.5	67.9	3.4
	3	31.0	1.8	67.2	0.0
	4	30.2	0.8	69.0	0.0
	5	29.0	1.6	65.8	3.5
	AVG	28.8	2.0	66.3	2.8
PLATES AFTER 12/13 HOURS CURING	1	29.5	1.0	69.5	0.0
	2	18.9	2.5	75.3	3.3
	3	32.5	1.5	65.9	0.0
	4	28.8	0.7	67.1	3.3
	5	30.9	1.0	68.1	0.0
	AVG	28.1	1.3	69.2	1.3

**FIG. 3A** EFFECT OF 1% TTBLs ON INDUSTRIAL PASTE AND PLATE CURING – 2ND SAMPLE

CONTROL SAMPLE						
SAMPLE	SAMPLE NO.	PB	A-PBO (TETRA)	B-PBO (ORTHO)	TETRABASI C	TRIBASIC
PASTE AT END OF MIXING		13.8	25.8	5.1	5.1	50.3
	AVG	13.8	25.8	5.1	5.1	50.3
PASTED PLATE AT END OF TUNNEL		15.6	28.2	2.4	10.6	43.3
	AVG	15.6	28.2	2.4	10.6	43.3
FULL RACK IN CHAMBER		16.5	28.5	13.8	0.0	41.2
	AVG	16.5	28.5	13.8	0.0	41.2
AFTER 2 HOURS IN CHAMBER		17.1	27.7	8.0	2.8	44.4
	AVG	17.1	27.7	8.0	2.8	44.4
AFTER 4 HOURS IN CHAMBER		14.6	22.6	3.1	16.2	43.5
	AVG	14.6	22.6	3.1	16.2	43.5
AFTER 6.5 HOURS IN CHAMBER		17.2	24.8	2.4	14.9	40.7
	AVG	17.2	24.8	2.4	14.9	40.7
AFTER 8.6 HOURS IN CHAMBER		18.6	19.8	16.1	3.3	42.2
	AVG	18.6	19.8	16.1	3.3	42.2
AFTER 12.5 HOURS IN CHAMBER		12.0	17.5	4	29	37.4
	AVG	12.0	17.5	4	29	37.4
AFTER 16.5 HOURS IN CHAMBER		3.2	14.5	1.1	59.6	21.6
	AVG	3.2	14.5	1.1	59.6	21.6
AFTER 20.5 HOURS IN CHAMBER		4.7	25	14.85	43.5	25.1
		0	15	1.1	75.3	8.6
	AVG	2.35	20	7.975	59.4	16.85
AFTER 24.5 HOURS IN CHAMBER		0	15	1.1	75.3	8.6
	AVG	0	15	1.1	75.3	8.6
AFTER 28.5 HOURS IN CHAMBER		0	15.4	1.3	76.8	6.6
	AVG	0	15.4	1.3	76.8	6.6

FIG. 3B

EFFECT OF 1% TBLS ON INDUSTRIAL PASTE AND PLATE CURING – 2ND SAMPLE

## CONTROL SAMPLE

SAMPLE	SAMPLE NO.	PB	A-PBO (TETRA)	B-PBO (ORTHO)	TETRABASIC	TRIBASIC
PASTE AT END OF MIXING		11.4	10.9	2.7	53.2	21.9
		17.8	6.7	0.8	69.1	5.6
		18.7	6.3	0.0	50.0	25.0
	AVG	15.97	8.0	1.2	57.4	17.5
PASTED PLATE AT END OF TUNNEL		8.2	13.0	3.2	54.7	20.9
		16.6	8.6	0.9	57.3	16.6
		19.8	4.7	0.0	67.4	8.1
	AVG	14.87	8.8	1.4	59.8	15.2
FULL RACK IN CHAMBER		8.2	13.5	0.9	62.3	15.2
		18.4	6.0	0.4	56.1	19.1
		18.3	9.2	0.8	66.2	5.5
	AVG	14.97	9.6	0.7	61.5	13.3
AFTER 2 HOURS IN CHAMBER		9	12.8	1.1	77.1	0.0
		12.6	5.7	2.7	70.6	8.5
		19.2	5.8	1.3	64.7	9.0
	AVG	13.60	8.1	1.7	70.8	5.8
AFTER 4 HOURS IN CHAMBER		7.3	6.9	1.0	73.0	11.8
		12.2	4.4	1.4	68.2	13.9
		6.5	9.6	1.0	75.5	7.4
	AVG	8.67	7.0	1.1	72.2	11.0
AFTER 6 HOURS IN CHAMBER		7.8	10.5	1.1	80.2	0.3
		11.9	2.7	1.4	70.0	14.0
		7.3	3.9	2.0	74.1	12.7
	AVG	9	5.7	1.5	74.8	9.0
AFTER 8 HOURS IN CHAMBER		6.4	5.2	1.6	73	13.8
		9.4	7.9	1.6	72.4	8.7
	AVG	7.9	6.55	1.6	72.7	11.25
	AFTER 10 HOURS IN CHAMBER	2.4	5.9	2.2	80	9.5
AFTER 12 HOURS IN CHAMBER		2.4	5.9	2.2	80	9.5
		1.9	3.4	2.4	83.7	8.5
		1.7	10.5	1.7	80.3	5.8
	AVG	1.8	6.95	2.05	82	7.15
AFTER 14 HOURS IN CHAMBER		7.4	8.4	1.2	72.4	10.6
	AVG	7.4	8.4	1.2	72.4	10.6
AFTER 16 HOURS IN CHAMBER		1.2	5.6	2	83.4	7.7
		13.1	8.4	1.3	72.4	4.8
	AVG	7.15	7.00	1.65	77.90	6.25
	AFTER 18 HOURS IN CHAMBER	1.3	4.4	3.3	83.7	7.3
AFTER 20 HOURS IN CHAMBER		0	7.2	0	86.5	6.4
	AVG	0.65	5.8	1.65	85.1	6.85
		1.7	6.9	2.3	81.1	7.9
		0.8	10.8	1.9	86.5	0
AFTER 22 HOURS IN CHAMBER		1.05	7.83	1.95	84.23	4.92
	AVG	1.3	4.4	3.3	83.7	7.3
AFTER 24 HOURS IN CHAMBER		1.3	4.4	3.3	83.7	7.3
		1.5	11.8	2.3	84.5	0
		1.3	8.7	2.4	80.3	7.3
	AVG	1.4	10.25	2.35	82.4	3.65
AFTER 26 HOURS IN CHAMBER		0.7	6.4	2.1	89.7	1.1
	AVG	0.7	6.4	2.1	89.7	1.1
AFTER 28 HOURS IN CHAMBER		0.6	11.5	1.9	86	0
		1.1	6	2.4	89.2	1.4
	AVG	0.85	8.75	2.15	87.6	0.7
	CHART TITLED "CURE EFFECT PHT 261"					

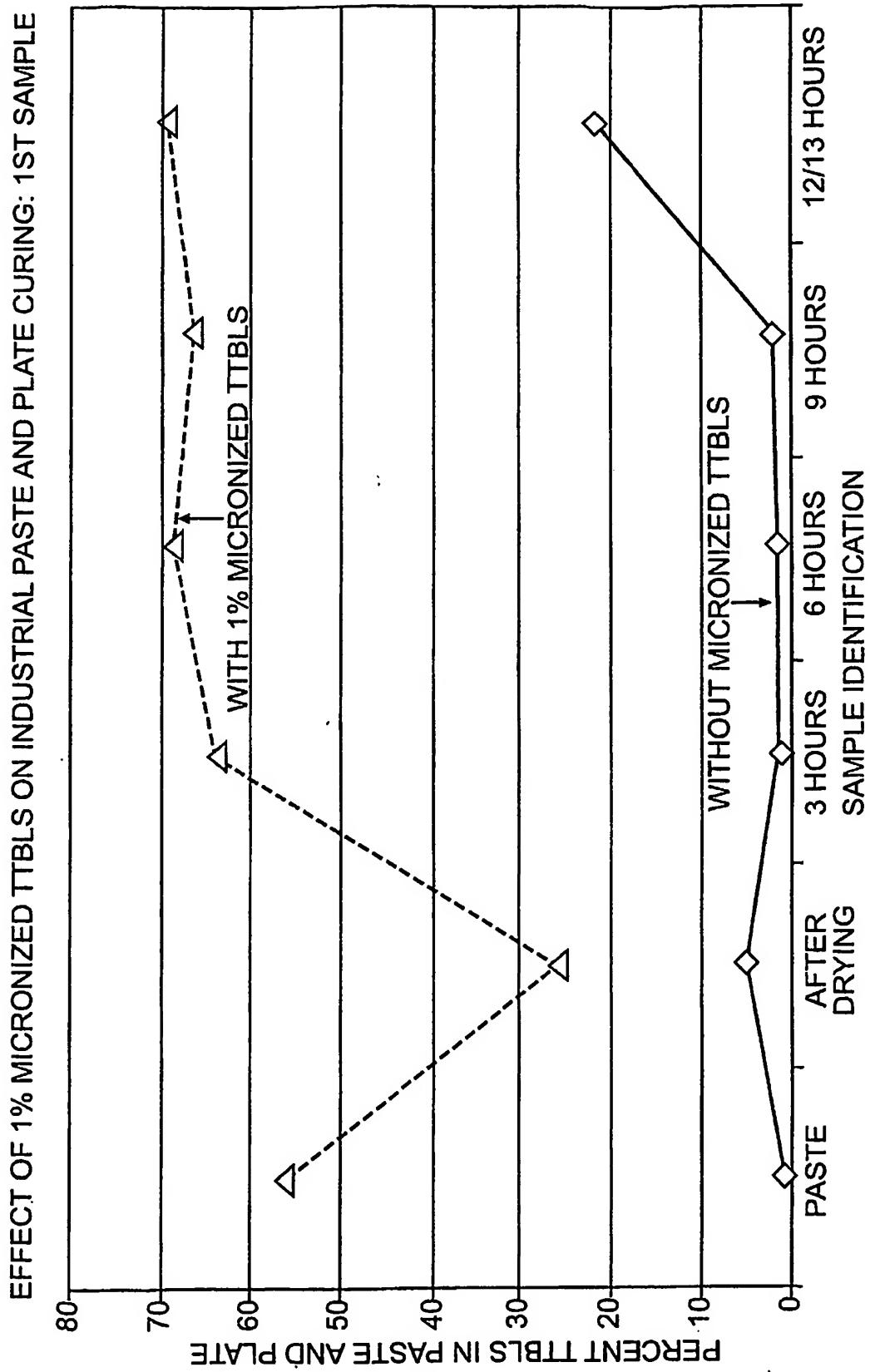


FIG. 4

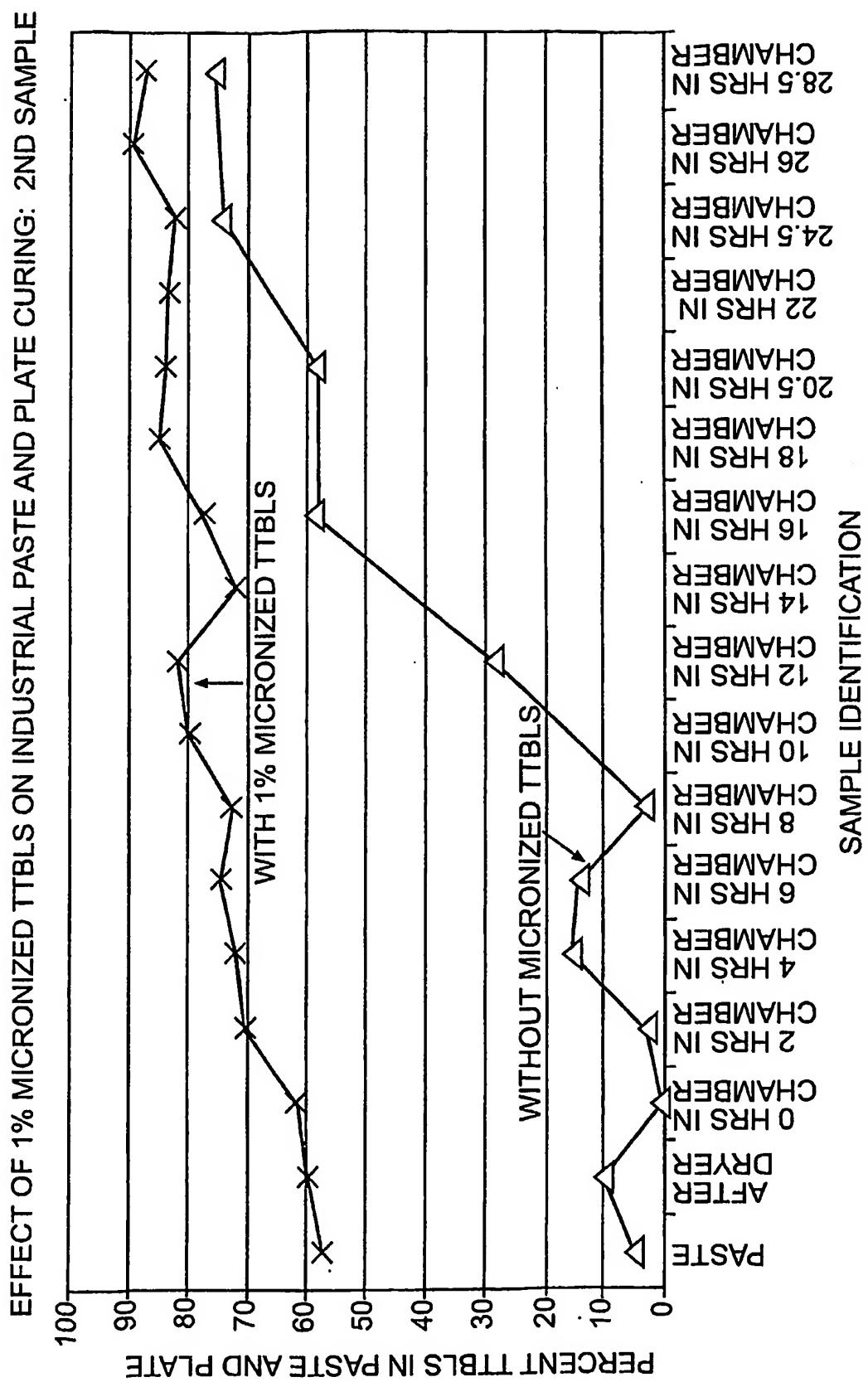


FIG. 5

**FIG. 6A** EFFECT OF 1% TTBLs ON AUTOMOTIVE PASTE AND PLATE CURING – THIRD SAMPLE

CONTROL SAMPLE						
SAMPLE	TRIAL	PB	A-PBO (TETRA)	B-PBO (ORTHO)	TETRABASIC	TRIBASIC
PASTE AT END OF MIXING	41	9.3	62.3	0.0	0.0	26.6
	40	3.1	72.5	1.4	0.0	23.1
	AVG	6.2	67.4	0.7	0.0	24.9
PASTED PLATE AT END OF TUNNEL DRYER	37	5.4	60.4	0.0	0.0	34.2
	38	18.7	49.3	0.7	0.0	31.3
	39	10.8	58.3	0.5	0.0	30.4
	AVG	11.63	56.0	0.4	0.0	32.0
TWO HOURS AFTER LOADING CURING CHAMBER						
	AVG					
SIX HOURS AFTER LOADING CURING CHAMBER	1		52.0	4.4	1.8	41.8
	2		57.1	9.1	0.0	33.7
	3		59.6	2.4	0.9	37.1
	4		54.4	8.2	1.6	35.8
	5		57.2	7.5	2.7	32.6
	AVG		56.1	6.3	1.4	36.2
8 HOURS AFTER LOADING CURING CHAMBER	12	7	63.1	1.0	0.0	28.8
	17	8.3	60.5	5.5	0.0	26.1
	18	6.8	59.1	5.1	0.0	28.9
	4		60.2	10.4	2.3	27.2
	5		61.6	3.2	1.9	33.3
	AVG	7.4	60.9	5.0	0.8	28.9
18 HOURS AFTER LOADING CURING CHAMBER	21	8.1	57.9	2.8	7.3	24.0
	23	7.5	58.2	3.6	7.9	24.0
	24	7.7	67.7	0.0	0.0	24.6
	AVG	7.8	63.0	1.8	4.0	24.3
24 HOURS AFTER LOADING CURING CHAMBER	29	5.1	44.4	0	35.7	14.8
	30	2.5	62.6	1	12.1	21.8
	AVG	3.8	53.5	0.5	23.9	18.3
END OF CURE	31	0	53.2	0.3	31.96	14.7
	32	0.8	50.7	0	36.2	12.3
	AVG	0.4	51.95	0.15	34.05	13.5

**FIG. 6B** EFFECT OF 1% TTBLS ON AUTOMOTIVE PASTE AND PLATE CURING – THIRD SAMPLE

EXPERIMENTAL SAMPLE						
SAMPLE	TRIAL	PB	A-PBO (TETRA)	B-PBO (ORTHO)	TETRABASIC	TRIBASIC
PASTE AT END OF MIXING	1	6.7	51.0	0.0	19.8	23.1
	2	14.9	48.3	0.9	12.2	23.7
	AVG	10.8	49.7	0.5	16.0	23.4
PASTED PLATE AT END OF TUNNEL DRYER	3	10.3	49.3	0.5	14.3	25.8
	4	8	47.7	4.1	15.9	24.3
	5	17.2	43.0	0.6	14.3	24.9
	42	13.8		1.2	21.4	22.1
	AVG	12.3	46.7	1.6	16.5	24.3
TWO HOURS AFTER LOADING CURING CHAMBER	6	12.9	43.3	0.6	21.8	21.3
	7	14.4	44.3	4.8	17.8	19.1
	8	12.3	49.2	1.4	18.4	18.8
	9	10.2	45.3	0.4	24.1	20.1
	AVG	12.4	45.5	1.8	20.5	19.8
SIX HOURS AFTER LOADING CURING CHAMBER	10	4.4	25.2	4.4	60.7	5.3
	AVG	4.4	25.2	4.4	60.7	5.3
8 HOURS AFTER LOADING CURING CHAMBER	11	6.5	21.6	1.0	66.3	4.5
	13	1.9	26.8	1.8	64.3	5.2
	14	4	29.0	2.5	56.9	7.6
	15	0	29.6	1.9	62.6	5.8
	16	3.9	24.8	1.9	63.7	5.7
	AVG	4.1	26.4	1.8	62.8	5.8
18 HOURS AFTER LOADING CURING CHAMBER	19	5.6	21.9	2.8	66.1	3.7
	20	5.3	22.3	3.4	64.3	4.3
	22	6.1	24.8	0.9	64.7	3.4
	3.7	25.1	2.3	68.9	0.0	
	AVG	5.7	23.53	2.35	66.0	2.9
24 HOURS AFTER LOADING CURING CHAMBER	25	1.3	24.5	0.8	69.9	3.5
	26	1.5	25.5	0	69.3	3.6
	27	2.6	28	1.1	61.8	6.5
	28	2.9	25.8	0	67.4	3.8
	AVG	2.075	25.95	0.475	67.1	4.35
END OF CURE	33	0	27.3	2.5	67.2	3
	34	3	28.4	1.3	64	3.2
	35	0.6	27.6	0	68.6	3.2
	36	0.6	26	3.1	64	6.2
	AVG	1.05	27.325	1.725	65.95	3.9

## EFFECT OF 1% MICRONIZED TTBLS ON AUTOMOTIVE PASTE AND PLATE CURING: THIRD SAMPLE

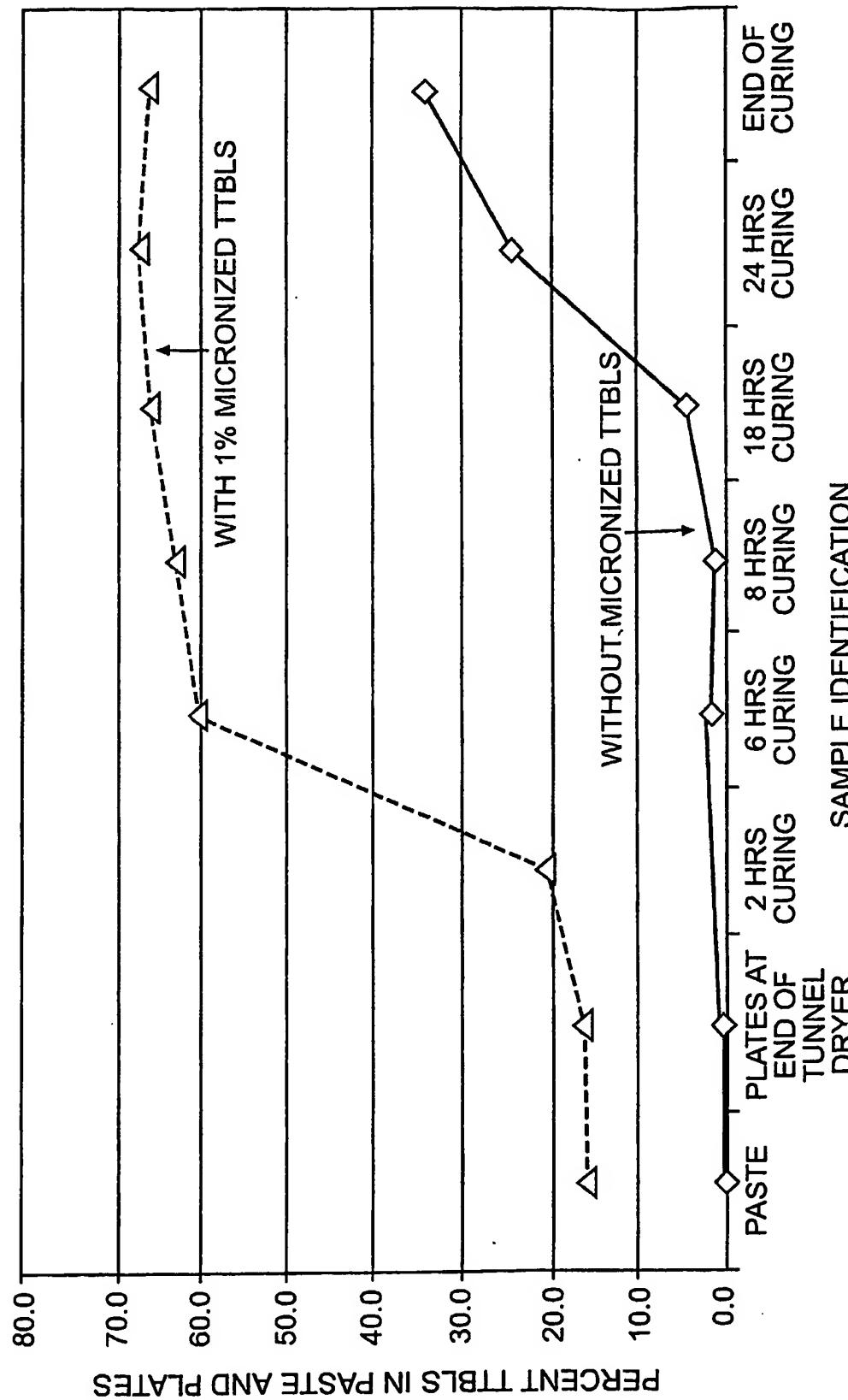


FIG.7

**FIG. 8**

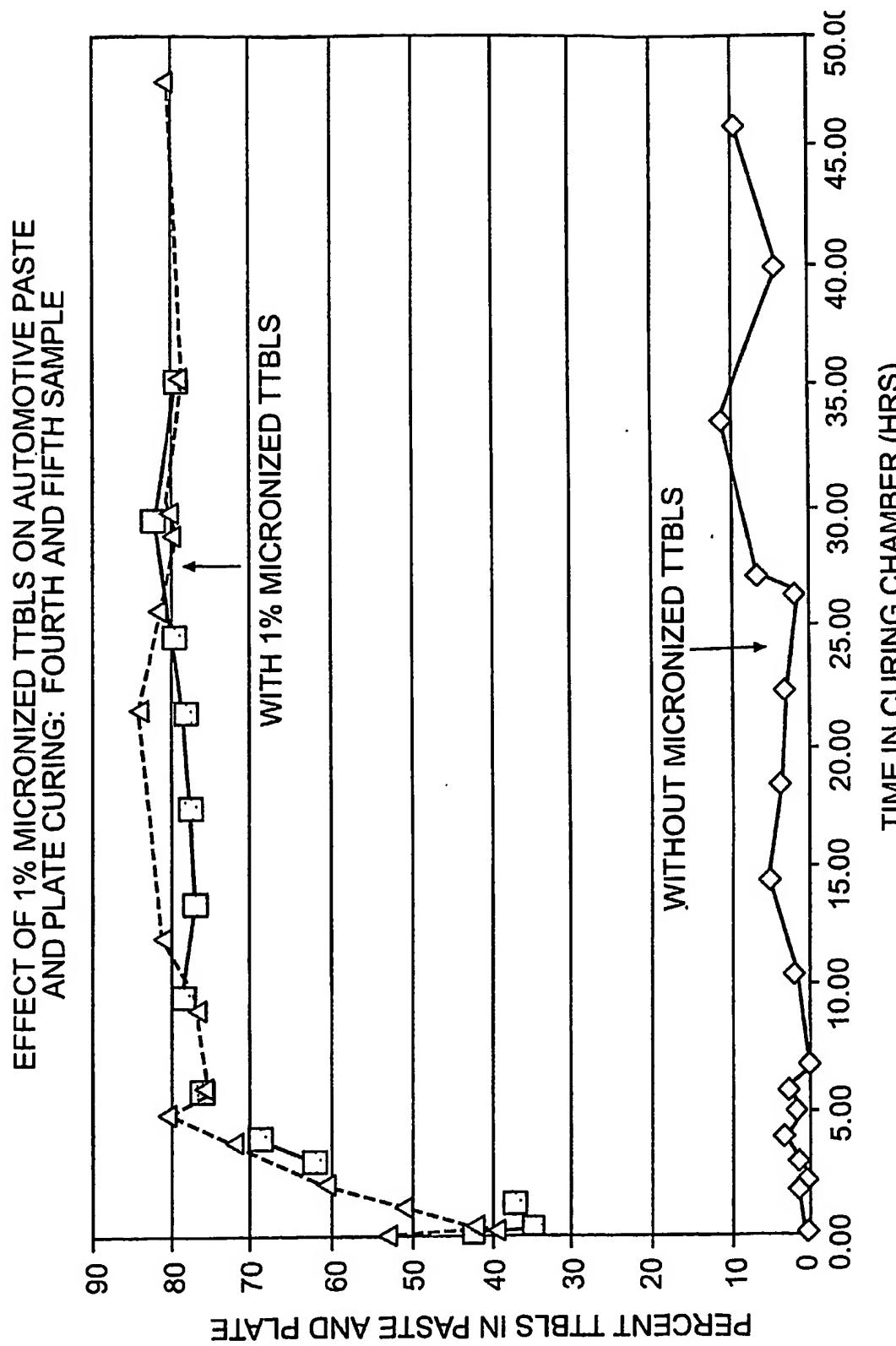
CONTROL SAMPLES (NO MICRONIZED TTBLS)	TIME (HRS)	PB	A-PBO (TETRA)	B-PBO (ORTHO)	TTBLS	TRBLS
CONTROL END OF TUNNEL	0	7.7	51.5	0	0	41.2
CONTROL END OF TUNNEL	0	6.5	43.4	9.2	0	35.2
CONTROL END OF TUNNEL	0	6	42.2	5.5	0	43.4
AVG	0	6.73	45.57	4.9	0	40.93
CONTROL RACK IN CURING CHAMBER	0.08	0.6	46	8	2.1	43.3
CONTROL RACK IN CURING CHAMBER	0.08	5.1	43.2	8.5	0	43.3
CONTROL RACK IN CURING CHAMBER	0.08	6.1	43.8	7.6	0	42.4
AVG	0.08	3.93	44.33	8.03	0.7	43.00
CONTROL	1.83	3.5	41.4	13.2	2.1	39.8
CONTROL	1.83	4.3	42.9	12.6	0.8	39.3
AVG	1.83	4.46	43.11	10.36	1.45	39.55
CONTROL	2.25	4.3	42.4	12.2	1	40.1
CONTROL	2.25	3.4	45.4	12.4	0	38.7
AVG	2.25	3.85	43.9	12.3	0.5	39.4
CONTROL	3	5.2	46.9	3.2	1.4	43.2
CONTROL	4	4.1	45.9	5.5	6.6	38
CONTROL	4	4	47.8	1.6	0	47.3
AVG	4	4.05	45.5	3.55	3.3	42.65
CONTROL	5	8.3	44	4.2	3.4	40.1
CONTROL	5	2.9	52.5	2.9	0	41.7
AVG	5	5.6	48.25	3.55	1.7	40.9
CONTROL	6	5.8	43	10.9	2.1	38.2
CONTROL	6	5.2	41.8	11.3	3.7	38
AVG	6	5.5	42.4	11.1	2.9	38.1
CONTROL	7	1.8	51.1	10.2	0	36.8
CONTROL	10.75	4.3	47.7	5	1.9	41
CONTROL	14.75	8.2	43.5	2.9	5.4	40.1
CONTROL	16.75	2.1	52.2	5.5	3.8	36.2
CONTROL	22.75	3	52.5	7.4	3.3	33.8
CONTROL	26.75	0	53.8	1.2	3.9	41.2
CONTROL	26.75	3.4	54.5	1.9	0	40.2
AVG	26.75	1.7	54.15	1.55	1.95	40.7
CONTROL	27.5	0	42.4	9.3	8	40.3
CONTROL	27.5	1.4	41.3	5.7	4.9	46.7
AVG	27.5	0.7	41.85	7.5	6.45	43.5
CONTROL	34	0	50.5	0	11.1	38.4
CONTROL	40.5	3.5	51.3	1.7	4.3	36.3
CONTROL	46.5	1.9	46.4	3.6	7.5	40.6

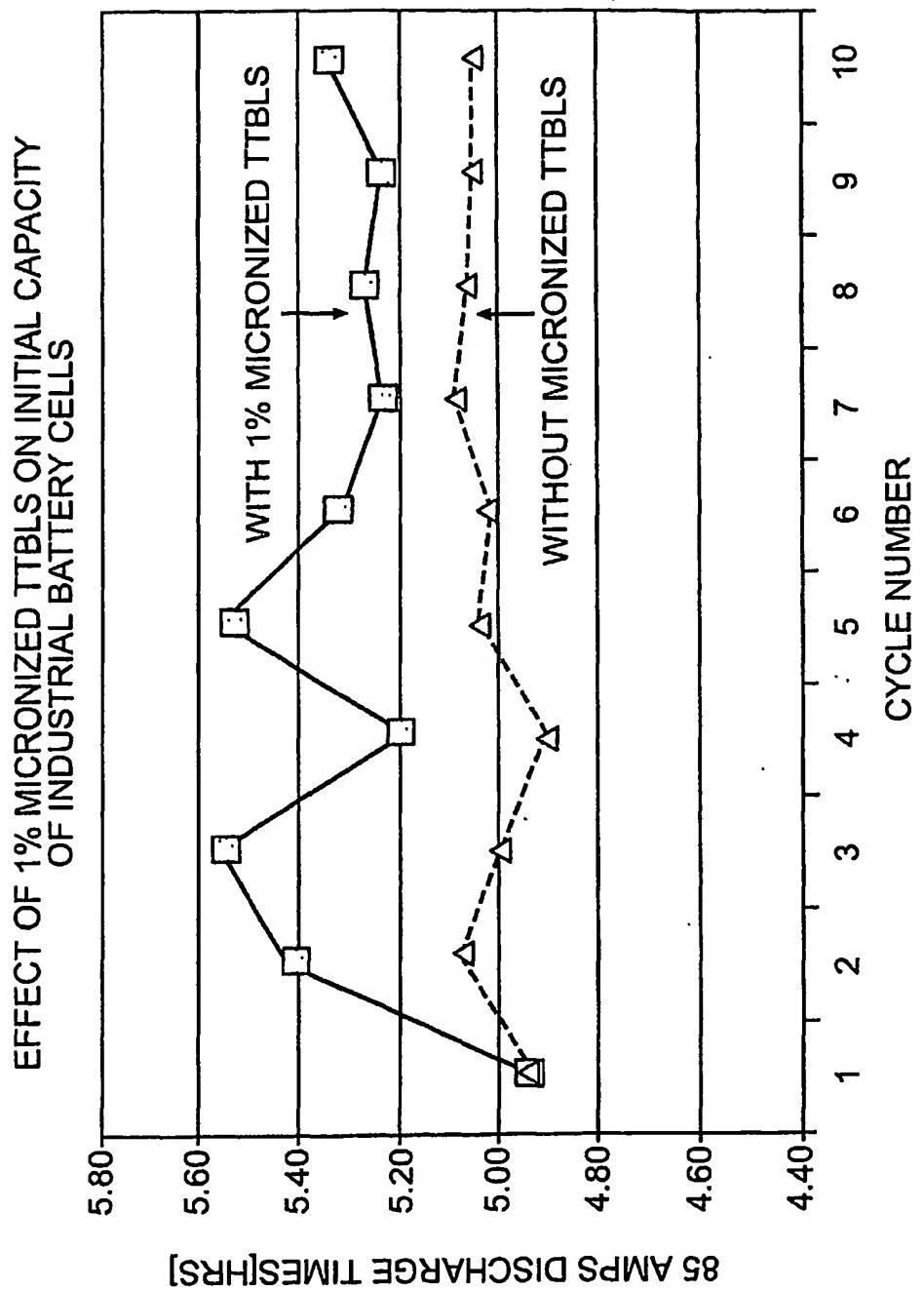
**FIG. 9**

EXPERIMENTAL SAMPLES, TRIAL 1 (1% MICRONIZED TTBLS)	TIME (HRS)	PB	A-PBO (TETRA)	B-PBO (ORTHO)	TTBLS	TRBLS
EXP. 1 PASTE MIX	0	0.9	35.1	1.2	46.9	15.8
	0	0	23.8	2.2	37.2	36.4
	AVG	0.45	29.45	1.7	42.05	26.1
EXP. 1 PASTE MIX 2	0	2.1	0	4.4	61	32.5
	0	0	0	5	61.9	33.2
	AVG	1.05	0	4.7	61.45	32.85
EXP. 1 END OF TUNNEL DRYER	0.33	0	31.7	5.3	34.7	28.2
EXP. 1	1.25	0.4	35.8	3.7	37	23.1
EXP. 1	3	2.1	21.8	2.3	60.4	13.5
	3	0	21.6	2.6	64.2	11.7
	AVG	1.05	21.7	2.45	62.3	12.6
EXP. 1	4	0	16	3.4	70.3	10.3
	4	1.8	19.1	2.7	68.1	8.3
	4	0.7	19.9	2.1	69.4	7.9
	AVG	0.83	18.33	2.73	69.27	8.83
EXP. 1	6	0	12.9	1.1	80.1	5.9
	6	0	8.2	7	72.8	12
	AVG	0	10.55	4.05	76.45	8.95
EXP. 1	9.75	0	5.9	10.3	77.7	6.1
	9.75	5.2	12.4	2.1	79.7	0.6
	AVG	2.6	9.15	6.2	78.7	3.35
EXP. 1	13.75	0	16.3	2.3	77.1	4.3
EXP. 1	17.75	0	16.8	1	78.5	2.8
	17.75	2.4	6.8	8.6	77	5.3
	17.75	0	15.7	2.3	77.7	4.3
	AVG	0.8	13.1	3.67	77.78	4.13
EXP. 1	21.75	1.3	4.6	9.1	78.5	6.4
EXP. 1	25	0.8	7.4	5	79.9	6.8
EXP. 1	29.75	0.5	7.5	0	87.3	4.7
	29.75	0	20.6	2.1	77.3	0
	29.75	0	13.8	2.8	81.8	0
	AVG	0.17	13.97	1.63	82.13	1.57
EXP. 1	35.75	0	19.5	2.5	78.5	0
	35.75	0	17.4	2.9	79.6	0
	AVG	0	18.45	2.7	79.05	0

**FIG. 10**

EXPERIMENTAL SAMPLES, TRIAL 2 (1% MICRONIZED TTBLs)	TIME (HRS)	PB	A-PBO (TETRA)	B-PBO (ORTHO)	TTBLs	TRBLs
EXP. 2 PASTE MIX	0	0	29.2	0.9	56.7	13.1
	0	1.1	28.7	1.3	53.4	15.5
	0	0	20.1	1.9	51.6	26.4
	0	0.37	26.00	1.37	53.90	18.33
EXP. 2 END OF TUNNEL DRYER	0.2	1.5	33.7	1.6	40	23.2
EXP. 2 RACK IN CURING CHAMBER	0.33	1.6	32.6	3	41.9	20.9
EXP. 2	1	1.9	28	1.5	51.5	17.2
EXP. 2	2	0	26.8	2.3	60.5	10.4
	2	0	26.6	0	62.2	11.2
	2	0	26.7	1.15	61.35	10.6
	4	0	15.3	3.7	78.7	2.4
EXP. 2	4	2.9	19.7	2.5	65.8	9.1
	4	1.45	17.5	3.1	72.25	5.75
	5	1.7	15	2.9	80.4	0
	5.5	1.7	14.6	3.3	75.8	4.4
EXP. 2	6	0	14.6	3.1	82.3	0
	6	0	15.4	2.9	78.4	6.4
	6	1.2	17.9	2.9	70.6	7.4
	6	0.4	15.97	2.93	76.10	4.60
EXP. 2	9.25	0.8	13.9	3.4	77	4.9
EXP. 2	12.25	0	15.1	3.6	81.3	0
EXP. 2	21.75	0	10.7	2.4	81.1	5.2
	21.75	0	6.2	1.6	87.2	5
	21.75	0	8.45	2	84.15	5.1
	26	0	4	5.8	84.4	5.6
EXP. 2	26	0.8	16.9	2.9	79	0.5
	26	0.5	16.5	3.3	79.7	7
	26	0.43	12.47	4.00	81.03	4.43
	29.25	0	18.7	1.9	79.5	0
EXP. 2	30.25	0	16.8	2	81	0
EXP. 2	35.75	0	18.2	2.9	78.9	0
	35.75	0.5	18.3	2.2	79	0
	35.75	0.25	18.25	2.55	78.95	0
	48.17	0	16.5	3.1	80.4	0

**FIG. 11**

**FIG. 12**

**FIG. 13****EFFECT OF 1% TTBLS ON INDUSTRIAL PASTE AND PLATE CURING**

PASTE MIX NO.	PB [WT.%]	A-PBO [WT.%]	B-PBO [WT.%]	TTBLS [WT.%]	TRBLS [WT.%]
MIX - 1	0.0	27.0	1.3	71.7	0.0
MIX - 2	2.8	15.5	0.9	79.4	1.4
MIX - 3	0.0	16.7	1.7	81.6	0.0
MIX - 4	1.7	21.3	1.3	75.7	0.0
MIX - 5	4.6	23.1	1.6	70.8	0.0
MIX - 6	0.0	29.0	1.1	69.9	0.0
MIX - 7	1.1	25.8	1.7	71.4	0.0
MIX - 8	1.6	25.2	0.8	72.5	0.0
MIX - 9	1.5	29.9	1.1	67.5	0.0
MIX - 10	5.7	28.5	0.8	65.1	0.0
MIX - 11	2.2	30.0	1.7	60.5	5.7
MIX - 12	1.3	27.0	1.7	69.9	0.0
MIX - 13	0.0	25.5	2.5	71.9	0.0
MIX - 14	0.0	26.3	1.8	71.9	0.0

**FIG. 14**

	1 <sup>ST</sup> RESERVE CAPACITY (MINUTES)	2 <sup>ND</sup> RESERVE CAPACITY (MINUTES)	3 <sup>RD</sup> RESERVE CAPACITY (MINUTES)	1 <sup>ST</sup> COLD CRANKING AMPS (AMPERES)	2 <sup>ND</sup> COLD CRANKING AMPS (AMPERES)	3 <sup>RD</sup> COLD CRANKING AMPS (AMPERES)	AMPERE- HOURS AT 20 HOUR RATE
WITHOUT	125.9	114.8	94.9	699	713	676	57.9
MICRONIZED	124.6	116.9	99.6	702	723	676	59.2
TTBLS	123.7	112.4	94.7	693	710	660	57
AVG	124.7	114.7	96.4	698	715	671	58.02
<hr/>							
WITH	126.7	132	126.7	705	746	666	64.7
MICRONIZED	127.3	130.5	124.2	705	742	675	63.3
TTBLS	128.1	131.1	126.7	701	732	685	63.78
AVG	127.4	131.2	125.9	704	740	675	63.92